## ENVIRONMENTAL OUTCOME

# **Nutrient Holding Time Study**

Regions: Lahontan, Central Valley, and Central

Coast

**Sampling Period:** June and July 2008

<u>Report</u>

**Objectives:** Determine whether refrigerating or

freezing water samples extends SWAMP required holding times for

some nutrient analyses.

MESSAGE: The holding time for Soluble

Reactive Phosphorous (SRP) may be extended up to four days for frozen

samples. Other constituents

showed possible analyte stability above the Reporting Limits dependent on concentration ranges, but failed Lab Quality Assurance resulted in inconclusive statistical comparisons.

<u>Site Locations</u>: Lahontan Region (Upper Truckee River (UTR) and West Fork Carson River (WFCR)); Central Valley Region (San Joaquin River at Airport (SJR) and Sacramento River at Freeport (SRF)); Central Coast Region (Franklin Creek (FC) and Orcutt Creek (OC)).

# WHAT IS THE MEASURE SHOWING?

Analytical holding times (48 hour, 4 day, 7 day, and 28 day) were statistically evaluated for three concentration ranges for multiple nutrients in both frozen and refrigerated ambient water samples. For Soluble Reactive Phosphorous (SRP) the results show that the holding time for frozen or refrigerated samples may be extended up to four days at all concentration ranges. Results for Ammonia and Total Nitrogen show that samples for these constituents should be analyzed within 48 hours. Results for remaining constituents measured (Nitrite, Nitrate + Nitrite, Nitrate, and Total Phosphorous) for both frozen and refrigerated samples were statistically inconclusive due to failed lab Quality Assurance; although frozen samples with mid to high concentrations ranges did appear more stable.

## **WHY THIS INFORMATION IS IMPORTANT?**

The Surface Water Ambient Monitoring Program collects samples for nutrient analysis to help assess the overall health of a water body. Transferring samples from the water body to the laboratory for analysis within the current required holding time is not always feasible because of logistical and budget concerns. Acid preservation is useful for extending the holding times of samples with high concentrations of nutrients, but acid preservation may compromise the integrity of samples containing low levels of nutrients. Validating alternate means of extending holding times (e.g. freezing) may confirm accurate nutrient analyses in samples from remote locations.

### WHAT FACTORS INFLUENCE THE MEASURE?

Increased temperature and pH in a water body facilitates the change from unionized ammonia to ionized ammonia gas and thereby increasing the ammonia measurements. High salinity levels can also have an impact on the ammonia levels in water samples. For this study, sampling technique, preservation methods, ranges in original concentration, and internal quality control impacted the resulting data.

#### **TECHNICAL CONSIDERATIONS:**

• Data source: Central Valley Water Board SWAMP





Number of Sites Number of Constituents

Total Number of Samples

Preservation Methods

Holding Times Evaluated 48

Six (2/region)

Seven

SRP, Nitrite, Nitrate + Nitrite, Ammonia, Nitrate, Total Phosphorous, and Total Nitrogen

Refrigeration or Freezing

San Joaquin River Watershed Unit SWAMP

Table 1. Resulting Holding Time Comparisons at Various Nutrient Analyte Concentrations

				Comparable Concentrations					
	Range of Constituent Concentration	Site Number#		Frozen Preservation			Refrigerated Preservation		
-		Number#		4 Days	7 Days	28 Days	4 Days	7 Days	28 Days
	Below Reporting Limit (0.050mg/L)	1, 2, 4, 5		Yes	No	No	Yes	No	No
SRP	0.050mg/L - 0.060mg/L	3	48 hours	Yes	Yes	Yes	Yes	Yes	No
	0.400mg/L - 0.500mg/L	6		Yes	Yes	Yes <sup>^</sup>	Yes <sup>^</sup>	Yes <sup>^</sup>	Yes <sup>^</sup>
	0.019mg/L - 0.029mg/L	2		Yes	No	No	No	No	No
Nitrite	0.028mg/L - 0.036mg/L	1, 3	48 hours	No	No	No	No	No	No
	0.138mg/L - 0.144mg/L	5		Yes	Yes	Yes	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
	0.239mg/L - 0.248mg/L	6		NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
go.	0.017mg/L - 0.024mg/L	4	48 hours	Yes	No	No	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
Nitrate + Nitrite	0.041mg/L - 0.049mg/L	1, 2		Yes	Yes	Yes	Yes	Yes	No
	1.474mg/L - 1.506mg/L	3		NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
litrat	24mg/L - 26mg/L	5		Yes	Yes	Yes	Yes	Yes	Yes
	30mg/L - 33mg/L	6		Yes°	Yes°	Yes°	Yes°	Yes°	Yes°
nia	0.014mg/L - 0.021mg/L	3, 4	48 hours	No	No	No	Yes	No	No
Ammonia	0.021mg/L - 0.032mg/L	1, 2, 5		No	No	No	No	No	No
An	0.099mg/L - 0.119mg/L	6		Yes	Yes	Yes	Yes	Yes	No
	0.010mg/L - 0.024mg/L	1, 2, 4	48 hours	No	No	No	No	No	No
Nitrate	1.438mg/L - 1.473mg/L	3		Yes	Yes	Yes	Yes	Yes	Yes
i i	23mg/L - 26mg/L	5		Yes	Yes	Yes	NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
	30mg/L - 33mg/L	6		Yes^°	NA*°	NA*°	NA*°	NA*°	NA*°
	0.146mg/L - 0.204mg/L	1, 2, 4		No Frozen Samples Analyzed			No	Yes	No
Total N	2.0mg/L - 2.5mg/L	3	7 days (US EPA Recommended)				Yes	Yes	Yes
Tot	24mg/L - 27mg/L	5					Yes	Yes	Yes°
	32mg/L - 35mg/L	6					Yes°	Yes°	Yes °^
۵	0.030mg/L - 0.053mg/L	1, 2, 4, 5	48 hours	No Frozen Samples Analyzed			No	No	No
Total	0.156mg/L - 0.182mg/L	3					NA <sup>*</sup>	NA <sup>*</sup>	NA <sup>*</sup>
	0.822mg/L - 2.561mg/L	6					Yes°	Yes°	Yes°
^Spike recovery outside control limits. Spike added less than one half sample concentration. LCS and Method Blank are in control.		°Field Blanks did not meet SWAMP QA/QC however data not considered invalid because the sample concentration was 10X greater than the field blank result							
	#See Table 2 *Lab QA Failed			= no recommendation of hold time extension				= failed	

Table 2. Specific Conductivity Measurements at Each Site.

Site Number	Region	Site Location	SC (uS/cm)
1	Lahontan	Upper Truckee River	30
2	Lahontan	West Fork Carson River	50
3	Central Valley	San Joaquin River at Airport Way	576
4	Central Valley	Sacramento River at Freeport	142
5	Central Coast	Franklin Creek	1749
6	Central Coast	Orcutt Creek	2714



